

FINAL REPORT

INVESTIGATION OF THE INFLUENCE OF OZONE ON THE STABILITY  
OF DC-704 IN A DIFFUSION PUMP VACUUM SYSTEM

(1 November 1966 - 1 June 1967)

IITRI Project No. K6110  
Contract No. NAS5-10301

Prepared by  
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10 West 35th Street  
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For  
NASA  
Goddard Space Flight Center  
Greenbelt, Maryland

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## PREFACE

This program was conducted for the NASA-Goddard Space Flight Center with Mr. W. F. Hardgrove as NASA's Technical Director. At IIT Research Institute the program was directed by Mr. Frank Iwatsuki, Manager, Fluid Systems and Lubrication and Mr. Jerry Farrell, Project Engineer. Other IIT Research Institute personnel who have contributed to the technical efforts of the program are H. J. O'Neill and T. Kirch.

## ABSTRACT

This program was conducted to determine the influence of ozone on the stability of DC-704 in a diffusion pump vacuum system. One objective was to duplicate the explosion which occurred in the six-inch Kirney diffusion pump during the previous study\* using DC-704 fluid when ozone was leaked into the system. This objective was achieved, although the quantity and period of ozone leakage into the system were different.

Another objective of the program was to study the influence of various system parameters such as ozone leak rate, liquid nitrogen baffle usage, diffusion pump fluid usage, and diffusion pump design on the stability of DC-704 in a diffusion pump vacuum system when ozone is leaked into the system. This objective was not achieved because of the length of time and effort expended in duplicating the explosion of the previous program as well as the unpredictable nature of the results generated when all system parameters were held constant.

The stability of new DC-704 fluid in a diffusion pump vacuum system was studied when ozone was leaked into the system at very low leak rates for eight (8) hour periods. The influence of various rates of ozone leakage into a diffusion pump vacuum system containing DC-704 which had been used for as much as 143 days was studied during extended periods of ozone leakage into the system.

The results of these studies tend to verify the conclusion reached in our previous study that ozone, under the proper conditions, will generate an explosive reaction in a diffusion pump vacuum system using DC-704 fluid. These results also indicate the reaction generated in DC-704 fluid is not readily generated or duplicated in an operating diffusion pump.

Future work in this area should be directed towards the determination of the mechanism or mechanisms by which ozone can introduce an explosive reaction in DC-704. These studies should either be conducted prior to or in conjunction with any future ozone stability studies of DC-704 in an operating diffusion pump.

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\* NASA Contract No. NAS5-9632 entitled, "Investigation of the Explosion Hazard of Contaminated Diffusion Pump Fluids"

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# INVESTIGATION OF THE INFLUENCE OF OZONE ON THE STABILITY OF DC-704 IN A DIFFUSION PUMP VACUUM SYSTEM

## 1.0 INTRODUCTION

In 1965 IIT Research Institute conducted a study under NASA Contract No. NAS5-9632 to investigate the effect of contamination on the stability of DC-704 in diffusion pump vacuum systems. Prior to the initiation of this program, an explosion occurred in the Vertical Optical Bench at NASA-Goddard Space Flight Center. The cause of this explosion could not be definitely pinpointed; however, the possibility existed that very small amounts of contamination may have been present in the system at the time of the explosion.

During the investigation of the influence of contamination on DC-704 stability, the following areas were studied:

- The spontaneous ignition temperature of new, used, and contaminated DC-704 fluid
- The oxidation stability of new and contaminated DC-704 fluid in an air environment
- The stability of DC-704 in a diffusion pump when ozone was leaked into the system

The results of this study showed DC-704 to be extremely stable under normal diffusion pump conditions. The spontaneous ignition temperature was a minimum of 875°F and the fluid was thermally stable in air at 500°F. Catalytic studies indicated DC-704 to be stable in the presence of metallic contamination at elevated temperatures. In addition, an extensive field survey of diffusion pump users showed that only two occurrences of explosions under high vacuum steady state conditions have occurred. However, during the investigation of the influence of ozone on DC-704 stability, small quantities of ozone were leaked into a six-inch diffusion pump vacuum system and an explosion occurred several hours later. However, very little was known about the conditions existing in the diffusion pump at the time of the explosion, since the explosion occurred at night and automatic equipment for the recording of fluid temperature and system pressure was not included in the system. Therefore, this study was initiated to study the influence of ozone on the stability of DC-704 in a diffusion pump vacuum system.

This program included two (2) series of stability studies conducted in a six-inch diffusion pump vacuum system using DC-704. The first of these studies consisted of leaking small quantities of ozone into the vacuum system for brief periods of time and observing its influence on relatively new DC-704 fluid. In the second series of tests, DC-704 which had seen more extensive usage was subjected to various rates of ozone leakage over extended periods of time.

## 2.0 CONCLUSIONS

- 2.1 Ozone has detrimental influence on DC-704 in an operating diffusion pump system, and under proper conditions will result in an explosive reaction.
- 2.2 The exact mechanism by which ozone attacks DC-704 in an operating diffusion pump is not known.

### 3.0 EXPERIMENTAL EQUIPMENT AND PROCEDURES

Two (2) series of ozone stability tests were conducted on DC-704 diffusion pump fluid. These tests were conducted in the six-inch diffusion pump system shown in Figures 1 and 2. The first series of tests were conducted using a relatively new DC-704 fluid and short periods of ozone leakage into the system. The second series of tests were conducted using a conditioned DC-704 fluid. This fluid had been used for approximately 53 days prior to installation into the six-inch Kinney system. In addition, a large rate of ozone leakage was used during this phase, and leakage was continued over a much longer period of time.

#### 3.1 Vacuum System Used for Ozone Stability Studies

Figure 1 shows the physical arrangement of the vacuum system used for the ozone stability studies. Figure 2 is a schematic representation of the system. The system was pumped by a six-inch Kinney Model KDP-6 Diffusion Pump. The system also included a fifteen-inch glass bell jar, a liquid nitrogen baffle, a high vacuum valve, a water cooled cold cap, a mechanical roughing pump, and a liquid nitrogen cold trap. System pressures were monitored by a compensated thermocouple gauge in the foreline, and by ionization gauges above and below the orifice plate in the chamber. In addition, the sampling apparatus shown in Figure 3 was designed and attached to the diffusion pump for removing liquid samples from the operating diffusion pump.

The sampling apparatus, as can be seen in Figure 3, resembles a syringe. It consisted of a 3/16-inch outside diameter by 1/8-inch inside diameter stainless steel tube with a 1/8-inch diameter piston. Special seals were used in the syringe to maintain a vacuum as the syringe was inserted into the diffusion pump through a 3/4-inch ball type vacuum valve.

Other components of the vacuum system included an adjustable Granville-Phillips leak, an ozone generator, a stainless steel orifice plate, and two (2) chart recorders. The orifice plate consisted of a stainless steel plate with a 10 mm diameter sharp edged orifice at the center. This orifice plate was placed in the chamber to fix the pumping speed and thus allow the leak rate into the system to be calculated as a function of the pressure above the orifice plate.

As shown in Figures 1 and 2, the adjustable leak was attached to the bell jar and a tygon tube connected the leak to a horizontally mounted dewar. Therefore, any leakage into the system thru this leak must come from the dewar. The dewar



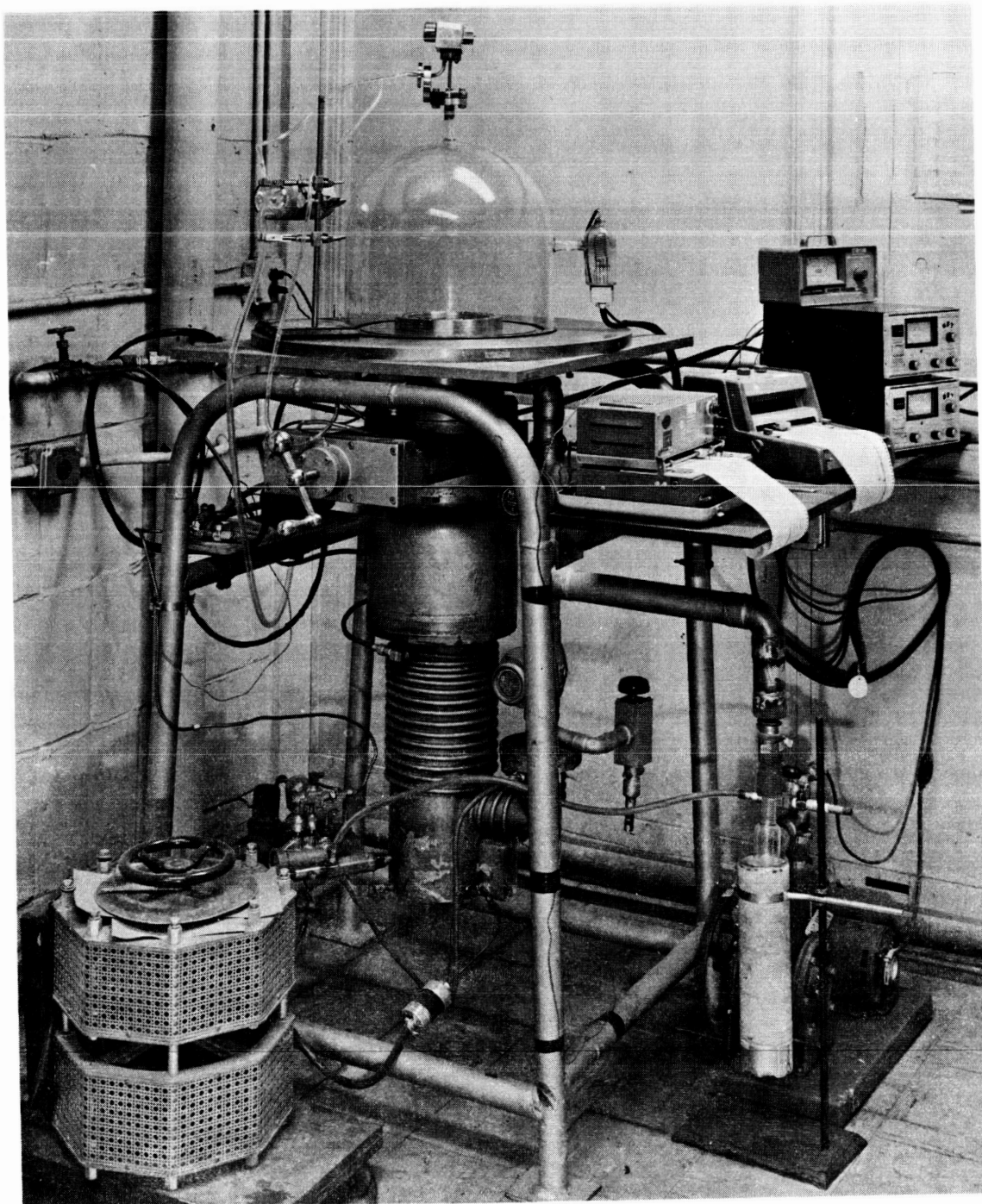


Figure 1 - Six-Inch Kinney Vacuum System used for  
Ozone Stability Studies

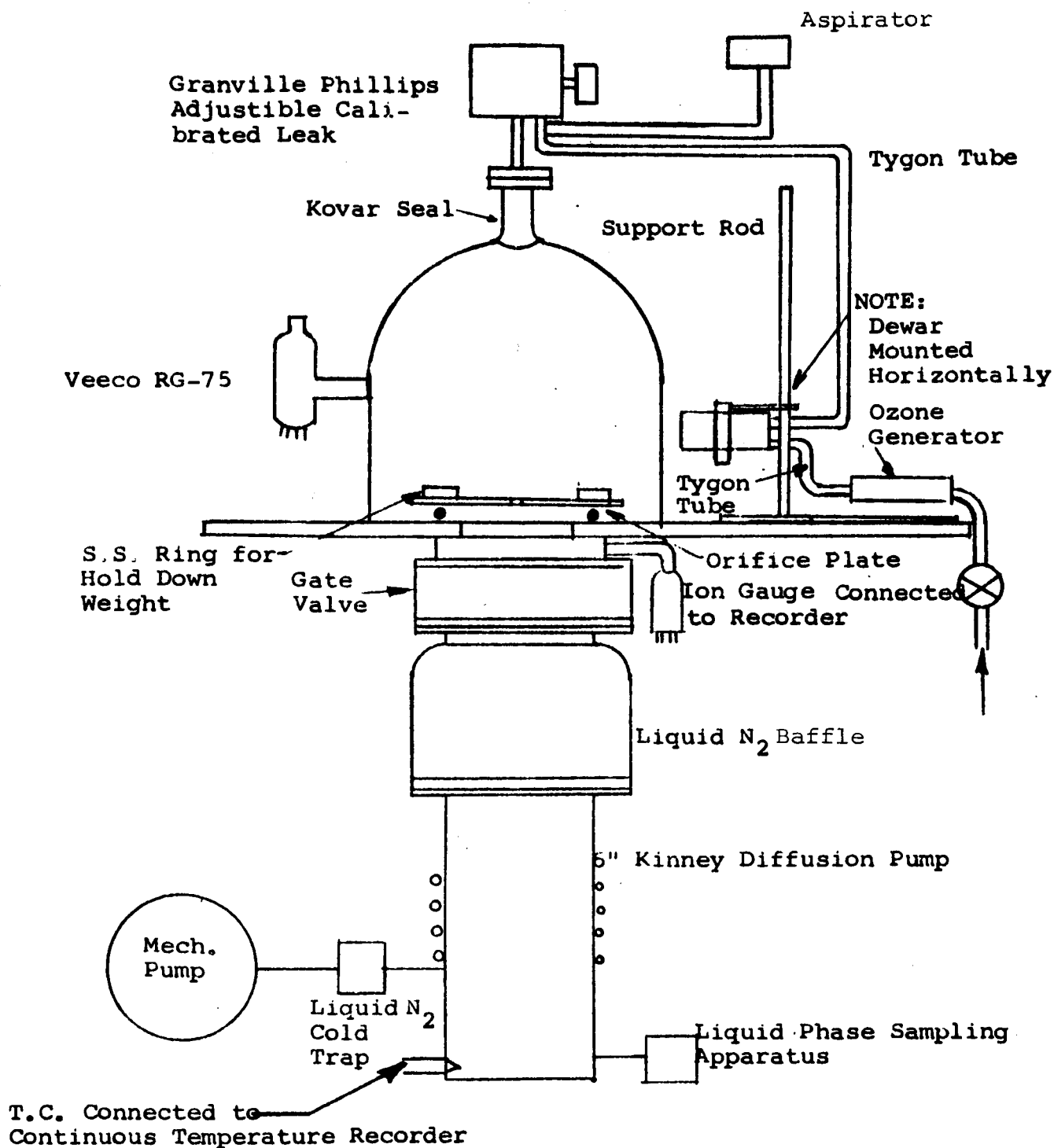


Figure 2 - Schematic Representation of Vacuum System Used for Ozone Studies with Aspirator

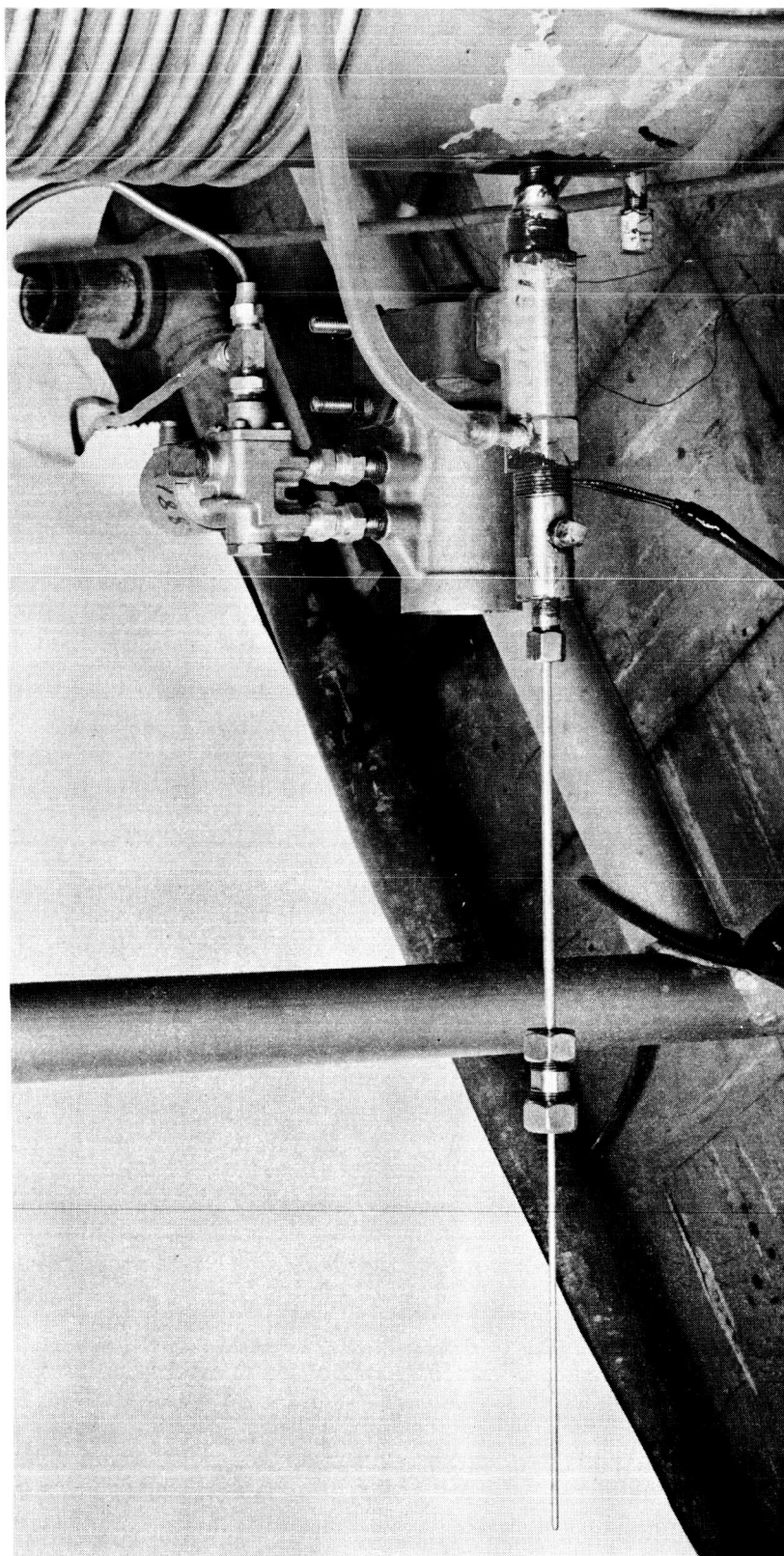


Figure 3 - Apparatus for Removing Liquid Phase Samples from Operating Diffusion Pump

was supplied with a mixture of 20 parts per million ozone in air. To insure that a mixture of ozone was always present in the tygon line leading to the adjustable leak, a glass tee was placed in the line leading to the adjustable leak and the tee was connected to the suction port of an aspirator.

The ozone generator is shown in Figure 4. This generator had been calibrated prior to initiation of the tests as 20 parts per million of ozone in air. This generator is a corona arc type generator.

Figure 5 shows the complete vacuum system used in the ozone stability studies. This figure is similar to Figure 1 except a plexiglass top cover was placed over the bell jar for protection. This plexiglass cover was replaced before initiation of the ozone leakage by a sheet metal cover.

Two (2) thermocouples were also installed in the diffusion pump to monitor the DC-704 fluid temperature at two points in the liquid phase. One thermocouple was located to read the fluid temperature near the center of the pump and the other thermocouple measured the fluid temperature approximately 1/2-inch inside the outer wall of the pump. This temperature as well as the system pressure below the orifice plate was continuously recorded by the chart recorders.

The recorder used to record the fluid temperature operated at 4-inches per hour, while the recorder used to record the system pressure operated at 2-inches per hour. A stepping switch was used with the ionization gauge to allow recording and monitoring of pressure changes.

### 3.2 Vacuum System for DC-704 Conditioning

The vacuum system shown in Figure 6 was used to condition 1000 ml of DC-704 fluid concurrently with the first series of ozone stability tests on new DC-704 fluid. This system consisted of a ten-inch NRC Model H-10-P diffusion pump with associated mechanical roughing pump, liquid nitrogen cold trap, ionization gauge, compensated thermocouple gauge in the foreline, and a thermocouple in the diffusion pump fluid for monitoring fluid temperature.

This system was used to condition the diffusion pump fluid by usage under steady state conditions, except for air releasing the system once each week. It was believed that fluid conditioned in such a manner for an extended length of time would probably be more susceptible to ozone attack than a relatively new fluid.

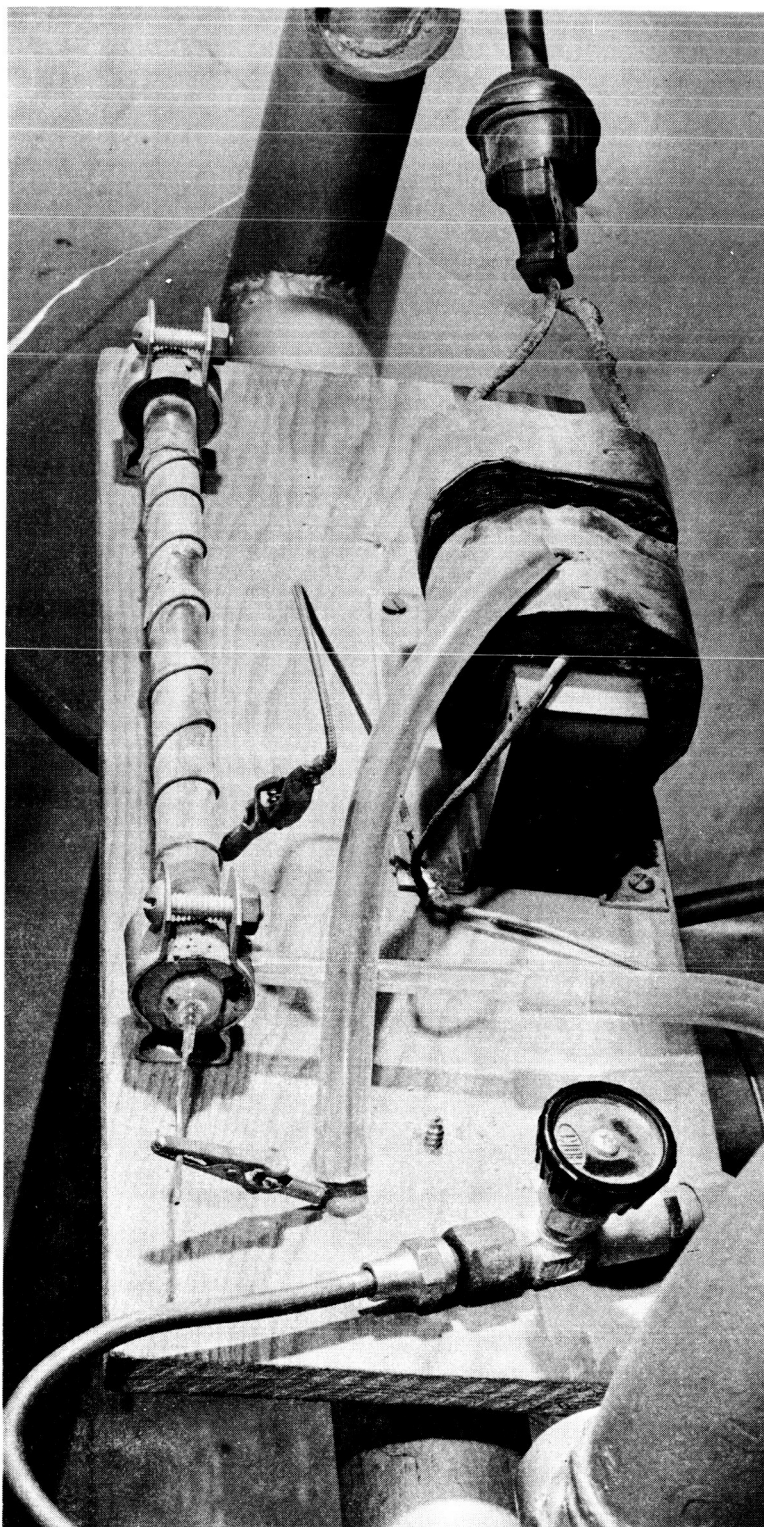


Figure 4 - Ozone Generator



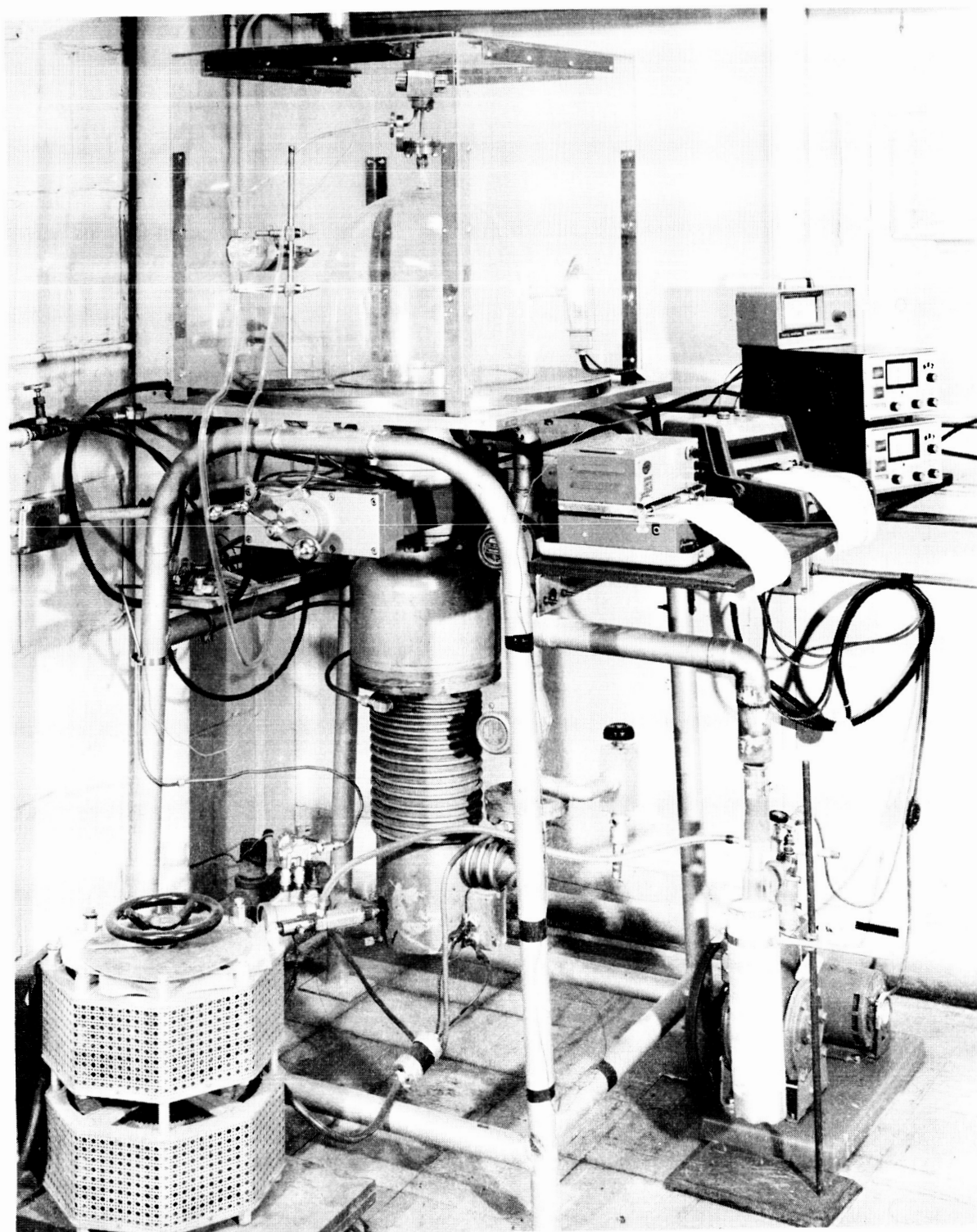


Figure 5 - Vacuum System for Stability Studies with Plexiglas Cover

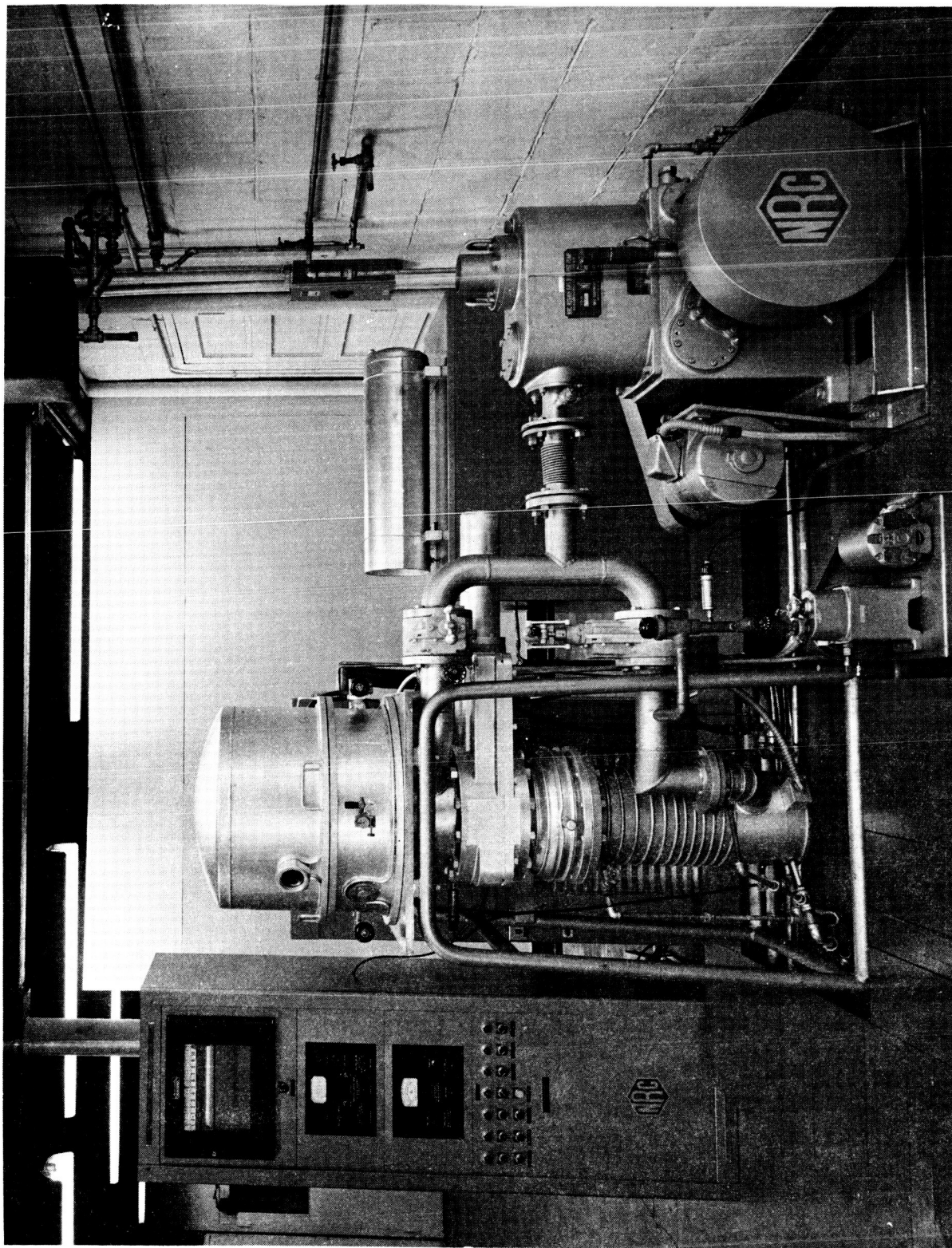


Figure 6 - Ten-Inch NRC Vacuum System Used to Condition DC-704 Fluid

The DC-704 fluid was used in this system for 53 days before it was removed and placed in the Kinney system for ozone stability tests.

### 3.3 Ozone Stability Tests

The Kinney vacuum system used for the ozone stability studies was supplied with 500 cc of new DC-704 fluid before pumping was initiated. The system was then pumped down with the adjustable leak closed and the liquid nitrogen baffle inoperative. After steady state was reached, the pressure above the orifice plate was  $3 \times 10^{-6}$  torr and below  $4 \times 10^{-7}$  torr.

The system was allowed to pump under steady state conditions for a period of one (1) week prior to the initiation of ozone leakage into the system. During this period the fluid temperature 1/2-inch inside the outer wall of the diffusion was approximately 370°F, while the temperature near the center of the pump was approximately 400°F.

After a week of steady state operation, a  $10^{-6}$  torr-liter per second leak of 20 parts per million ozone in air was established by opening the adjustable leak which was previously described. Ozone was allowed to leak into the system for a period of eight (8) hours at which time the adjustable leak was closed. This procedure was identical to the procedure used to generate an explosion during the ozone stability studies in the previous program, IITRI Project No. K6090 (NAS5-9632). Samples were removed from the liquid phase of the diffusion pump before initiation of the ozone leak, after termination of ozone leakage into the system, and at two hour intervals during the test.

The diffusion pump was then allowed to pump under steady state conditions for 11 days. After this period of time, a  $10^{-5}$  torr-liter per second leak containing 20 parts per million ozone was introduced. Ozone was allowed to leak into the system for a period of eight hours and then the adjustable leak was closed off. Samples of fluid were again removed from the liquid phase of the diffusion pump as in the first test.

After closing off the leak into the system, the diffusion pump was once more allowed to pump under steady state for approximately two weeks. During this period, fluid temperature and system pressure were monitored and recorded. In addition, fluid samples were removed daily for chemical analysis.



Since an explosion did not occur when ozone was leaked into the system with a relatively new DC-704 fluid, this fluid was removed from the system. Then 500 cc of the DC-704 fluid which had been used in the ten-inch NRC diffusion pump for a period of 53 days was installed in the Kinney system.

The ozone stability system was pumped down and held at steady state for a period of five days after installation of the conditioned fluid. Therefore, the fluid had essentially been used for 58 days prior to the introduction of ozone at the rate of  $10^{-5}$  torr-liters per second for a period of eight hours. Samples were removed as in previous tests during the period of ozone leakage into the system as well as each day during steady state operation. Since no apparent problems were caused by the eight hour leakage of ozone into the system, it was decided to pump the system under steady state for a longer period of time and then to initiate ozone leakage into the system in larger quantities and possibly over longer periods of time. During this period, the samples which had been removed from the system were subjected to chemical characterization.

The ozone stability system was thus allowed to operate under steady state conditions for an additional 52 days during which samples were removed daily for analysis. Therefore, the fluid in the system had been used for approximately 111 days at the end of this period. At this time, ozone was leaked into the system at the rate of  $10^{-4}$  torr-liters per second for eight hour periods each day for six days. In these tests as in all previous ozone tests it was required that the tube connecting the adjustable leak to the horizontally mounted dewar be evacuated each time before initiation of ozone leakage into the system.

Following these tests, the fluid had now accumulated 117 days of usage. To subject the fluid to a more severe test, the leak rate was adjusted to  $10^{-4}$  torr-liters per second and allowed to leak into the system continuously. This change in test procedure meant that only one sample of fluid could be taken each day to avoid dissipation of the required DC-704 fluid volume in the pump. In addition, the line connecting the leak to the dewar was not evacuated daily. Therefore, to insure that a continuous supply of 20 parts per million of ozone was actually present at the leak, an aspirator was installed in the system after the system had been in operation for 128 days. Ozone was continuously leaked into the system at  $10^{-4}$  torr-liters per second until an explosion occurred after the system, using the conditioned fluid, had been in operation for 143 days.

### 3.4 Chemical Characterization

The samples removed from the liquid phase of the operating diffusion pump as well as samples of fresh DC-704 fluid were analyzed by gas chromatography. These gas chromatographic studies were carried out isothermally at 270°C in a Loenco Model 70 dual-flow gas chromatograph. The coiled copper column used for analysis was 3/16-inch by 6-feet and contained three (3) weigh percent S.E.-30 (silicone gum rubber) on 60-80 mesh Chromosorb (ABS). Helium served as a carrier gas at an inlet pressure of 60 psig. The signal from the compensating electrometer was directed to a 0-1 multivolt recorder representing a signal current of  $10^{-9}$  amperes full scale. For all analyses, a total sample volume of 2 microliters of a 10% solution of the sample in chloroform was used. The attenuation of the signal was varied during the run to maintain the major peaks on the chromatogram and to detect the low level components.

Combined gas chromatography-mass spectrometry characterization was carried out on several used DC-704 samples in an attempt to identify the transient components which appeared in the gas chromatograms. However, detailed analyses of these components were complicated by the release of the silicone substrate from the columns in the gas chromatograph which gave high background in the mass spectrometer.

## 4.0 RESULTS

### 4.1 Stability of New DC-704 in a Diffusion Pump Vacuum System in the Presence of Small Quantities of Ozone

As described in the ozone stability test procedure, the ozone studies conducted on new DC-704 fluid in the diffusion pump system were for brief periods of time. In the first test, ozone (air-ozone mixture) was leaked into the system at the rate of  $10^{-6}$  torr-liters per second for a period of eight (8) hours. At this time the fluid was relatively new since it had only been used for one week. The leakage of ozone into the vacuum system using the relatively new fluid did not adversely influence the ability of the system to maintain the normal vacuum achieved prior to the initiation of the leak. Gas chromatography analysis of the samples removed during this test showed evidence of minor changes in three of the lighter components found in the DC-704.

Further leakage of the ozone-air mixture into the system at  $10^{-5}$  torr-liters per second for a period of eight hours after the fluid had been in use for 11 days also failed to produce any change in the efficiency of diffusion pump or to generate an explosive reaction.

### 4.2 Diffusion Pump Stability Studies with Used Fluid in the Presence of Ozone

The term "conditioned fluid" is used frequently in this report, and its meaning can be easily misinterpreted. As used in this report, conditioned fluid only means that the DC-704 fluid was previously used in a diffusion pump for a minimum of 53 days. The selection of 53 days was originally based entirely on its significance in the previous program, since the DC-704 fluid in the diffusion pump at the time of that explosion had accumulated approximately 53 days of pumping under steady state conditions.

However, on the present program it was not possible to use or condition DC-704 fluid in the Kinney pump under steady state conditions, since the pump was used for ozone stability tests. Therefore, a volume of fluid was conditioned or used in the 10-inch NRC system prior to installation in the Kinney pump.

The selection of 53 days initially or of an additional 90 days of use for conditioning is certainly not a fixed time. However, comparison of the gas chromatograms in Figures 14 thru 18 shows a definite increase in the light end components identified as peaks A, B, C, D, and E. Since none of these peaks were present in the gas chromatogram for the

new fluid and they appear to accumulate with time, we felt that the used or conditioned fluid might well be more susceptible to ozone attack. The significance of these peaks is discussed in Section 4.3. However, similar peaks were found in used fluids on the previous program in the absence of ozone.

The procedure used to evaluate the stability of used DC-704 fluid in the presence of ozone is described under ozone stability tests, Section 3.3. The results of all tests conducted on the used or conditioned DC-704 fluid indicate that no major changes occurred in the efficiency of the diffusion pump or in the condition of the fluid for the first 140 days of usage. During this period, a mixture of ozone and air was leaked into the system for periods of eight (8) hours on seven (7) different days and continuously for 24 days. A change in fluid temperature and system pressure occurred after 141 days of usage. The fluid temperature which had previously remained essentially constant at 370°F increased to 374°F. Approximately one-half hour after the fluid temperature increased to 374°F, the system pressure increased from  $8.8 \times 10^{-7}$  torr to  $1.2 \times 10^{-6}$  torr. The system pressure fluctuated between  $8.8 \times 10^{-7}$  torr and  $1.2 \times 10^{-6}$  torr on six occasions during the 43 hour period following its initial rise. Approximately 43 hours after the initial pressure increase, an explosion occurred in the system.

Figure 7 shows the condition of the sheet metal cover over the bell jar after the explosion. This cover was bolted down to the diffusion pump frame; therefore, the glass bell jar beneath the cover was undoubtedly blown upward against the cover. However, much of the distortion of the top cover would appear to have been caused by a shock wave. The possibility of this distortion being caused by fire was eliminated since the paint on the sheet metal showed no evidence of elevated temperature.

Figure 8 shows how the 15-inch glass bell jar was shattered by the explosion. No traces of the diffusion pump fluid or traces of carbon were found around the orifice plate as in the previous explosion.

Figures 9, 10, and 11 show the diffusion pump with the jet assembly removed, the interior of the diffusion pump, and the disassembled jet assembly following the explosion. Figure 9 indicates the relatively clean outer surface of the jet assembly except for localized carbon deposits. Figure 10 shows the carbon deposits inside the pump as well as the location of the christmas tree type superheaters used in the pump. Figure 11 shows the large deposits of ash and carbon found in the interior of the jet assembly. This figure also shows the change in deposits from a wet carbon at the top to a dry ash-like substance towards the lower end of the assembly. In

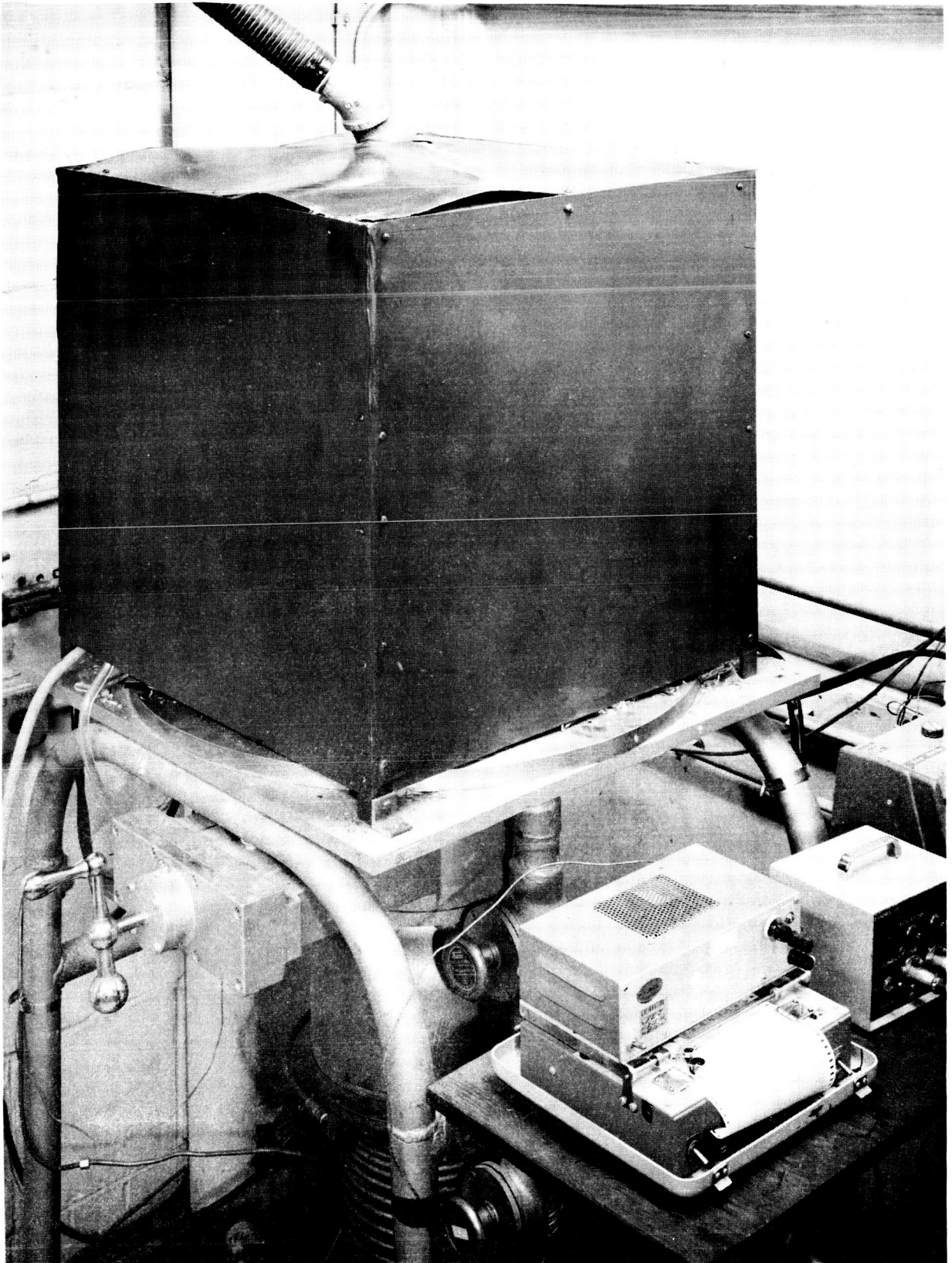


Figure 7 - Sheet Metal Cover for Vacuum System  
Following Explosion



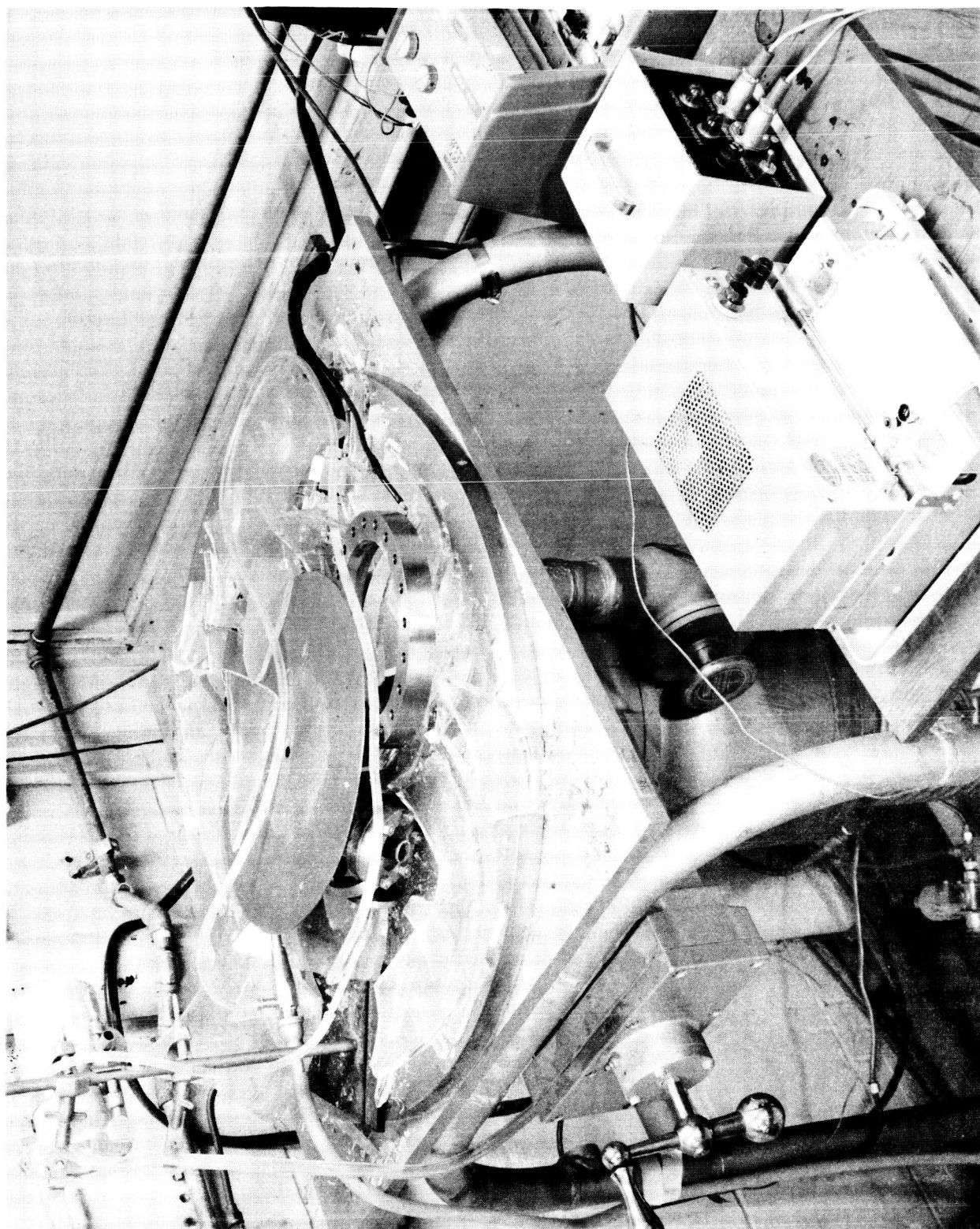


Figure 8 - Broken Bell Jar After  
Explosion

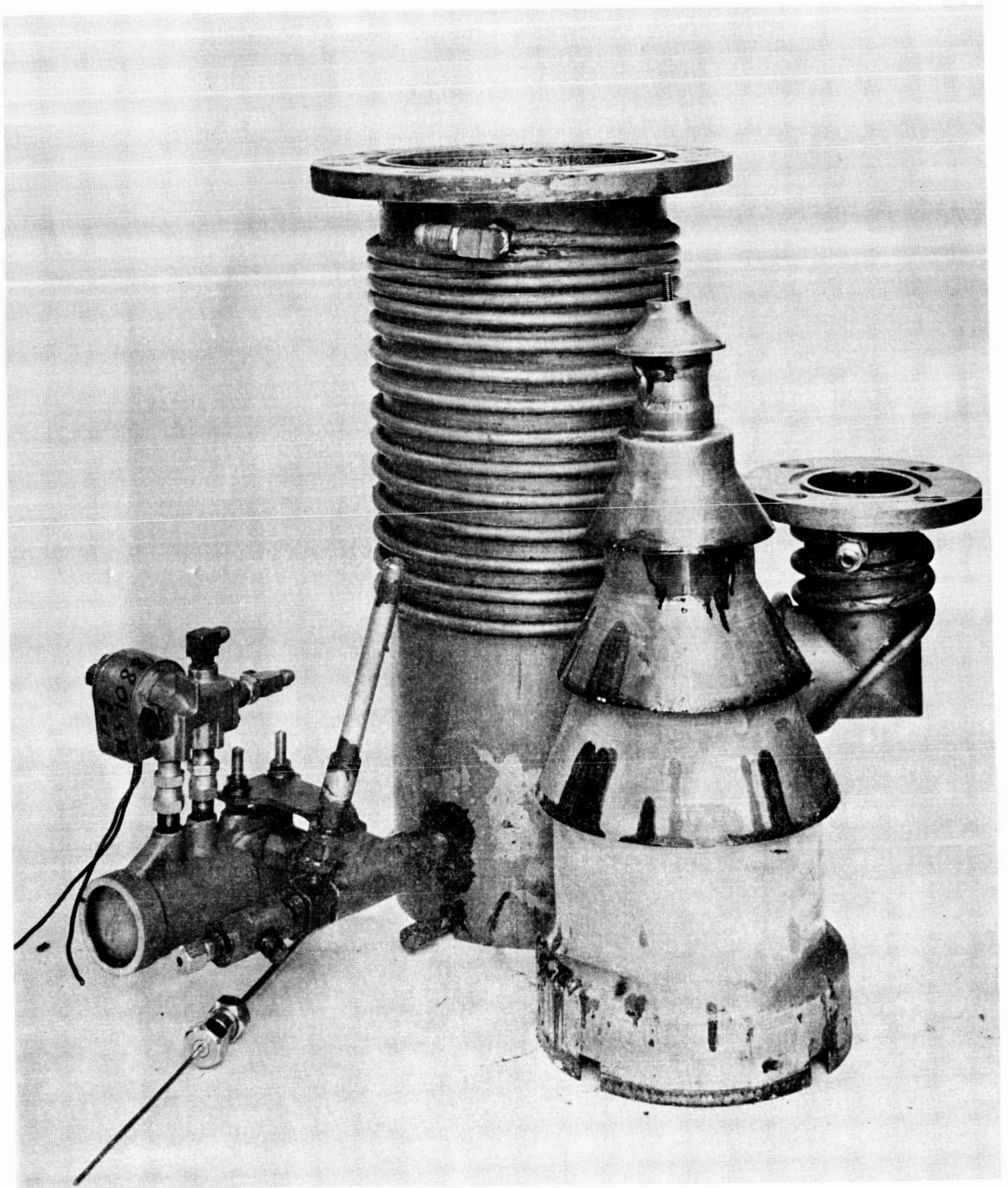


Figure 9 - Six-Inch Diffusion Pump with Jet Assembly Removed  
After Explosion

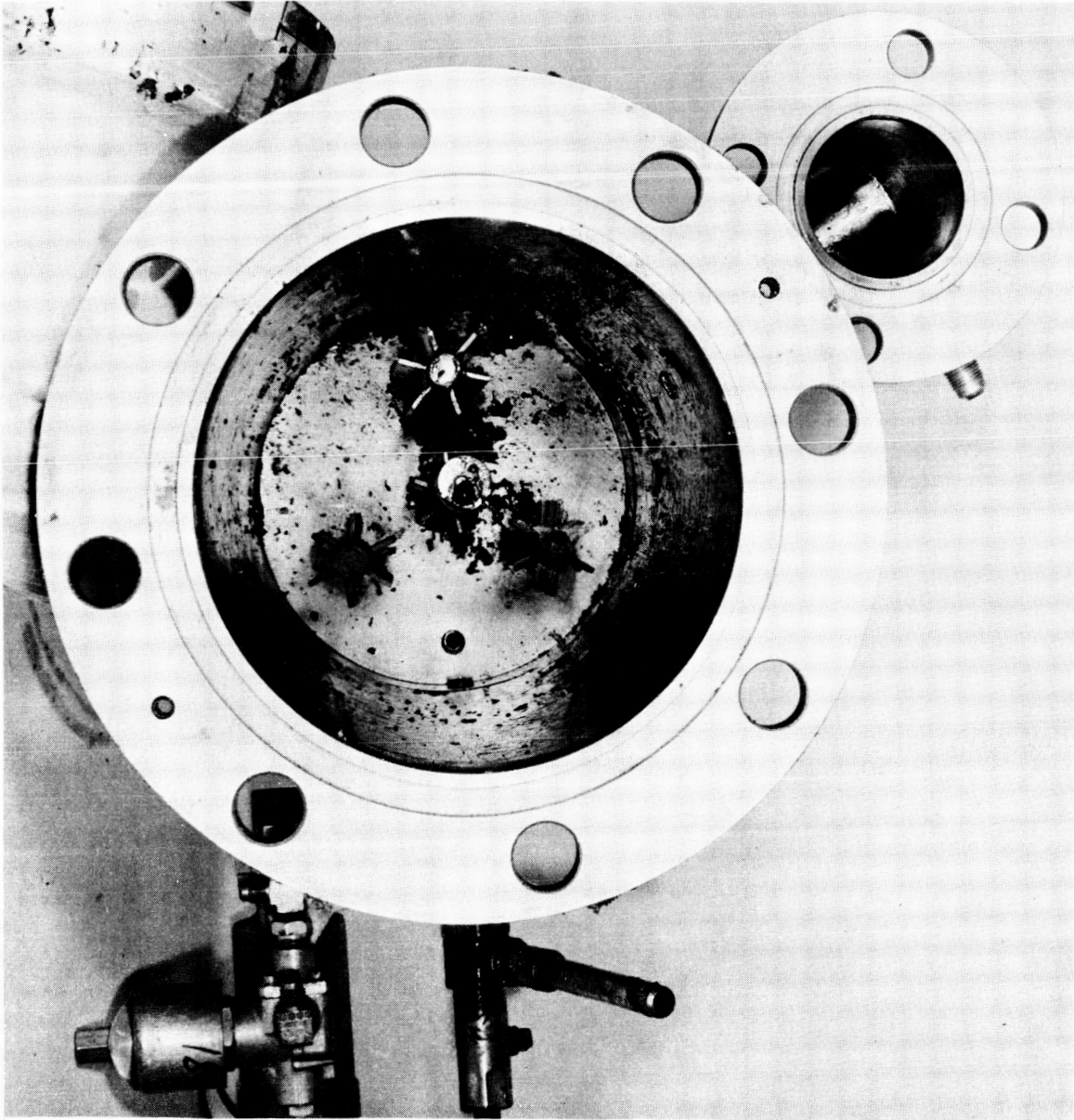


Figure 10 - Interior of Diffusion Pump After Explosion



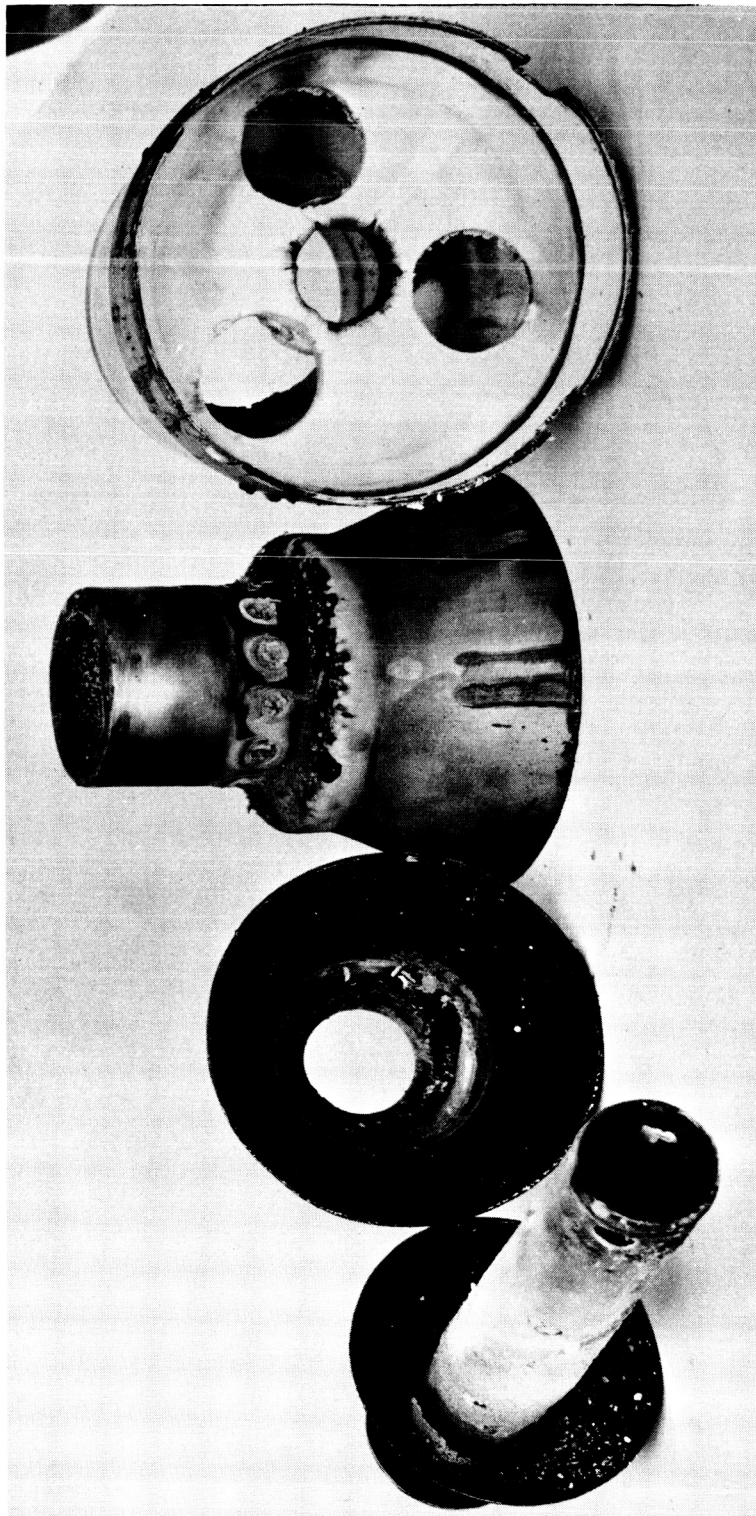


Figure 11 - Disassembled Jet Assembly After Explosion

addition, it can be observed that some of the jets are actually packed full of this ash material.

Figure 12 shows how the fluid temperature just inside the wall of the pump and the system pressure fluctuated during the 52 hour period preceding the explosion. These results indicate the pressure and temperature remained relatively constant for a period of 24 hours just preceding the explosion.

Figure 13 shows how the fluid temperature and system pressure fluctuated just prior to the explosion. The temperature decreased from 374°F to 370°F and then gradually increased to slightly over 400°F just prior to the explosion. These changes occurred during a period of approximately ten minutes. During this same period of time the system pressure increased rapidly from  $1.2 \times 10^{-6}$  torr to approximately  $2 \times 10^{-4}$  torr. The pressure remained essentially constant at  $2 \times 10^{-4}$  for approximately seven (7) minutes prior to the explosion. Although it is difficult to determine if the temperature change or pressure change occurred first, it would appear that they occurred almost simultaneously.

Examination of the system indicated the explosion definitely occurred in the lower section of the diffusion pump. Very little carbon was found in the foreline, and the glass cold trap in the foreline was not broken by the explosion.

#### 4.3 Gas Chromatography Analyses of the Samples Removed From Vacuum System Used for Ozone Stability Studies

The gas chromatographic analyses of the samples removed from the diffusion pump during the ozone stability studies and referenced with respect to time preceding the explosion are shown in Figures 14 - 18. The principle change that is readily apparent in the chromatograms is the appearance of several (5) volatile components in the fluid. These light (volatile) components are designated as peaks A, B, C, D, and E in the chromatograms and are not present in the new fluid (Figure 14). Of particular significance is the appearance of the transient peak D which can be readily observed in Figure 18. This component appeared in the pump fluid after 7½ hours of ozone introduction and remained at a very low concentration until the time of the 4°F temperature increase approximately 46 hours preceding the explosion. After this temperature rise, component D increased by a factor of 5 during this interval, while the other four components remained reasonably constant. A similar transient component was also observed in the fluid preceding the first explosion; however, the elution point of that component was just after the elution of component E rather than between C and E.

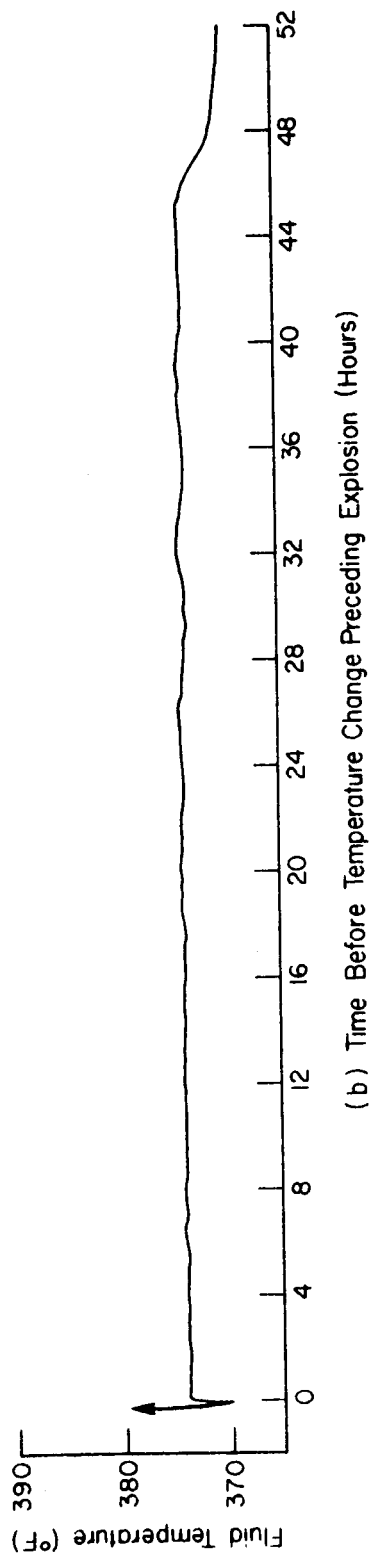
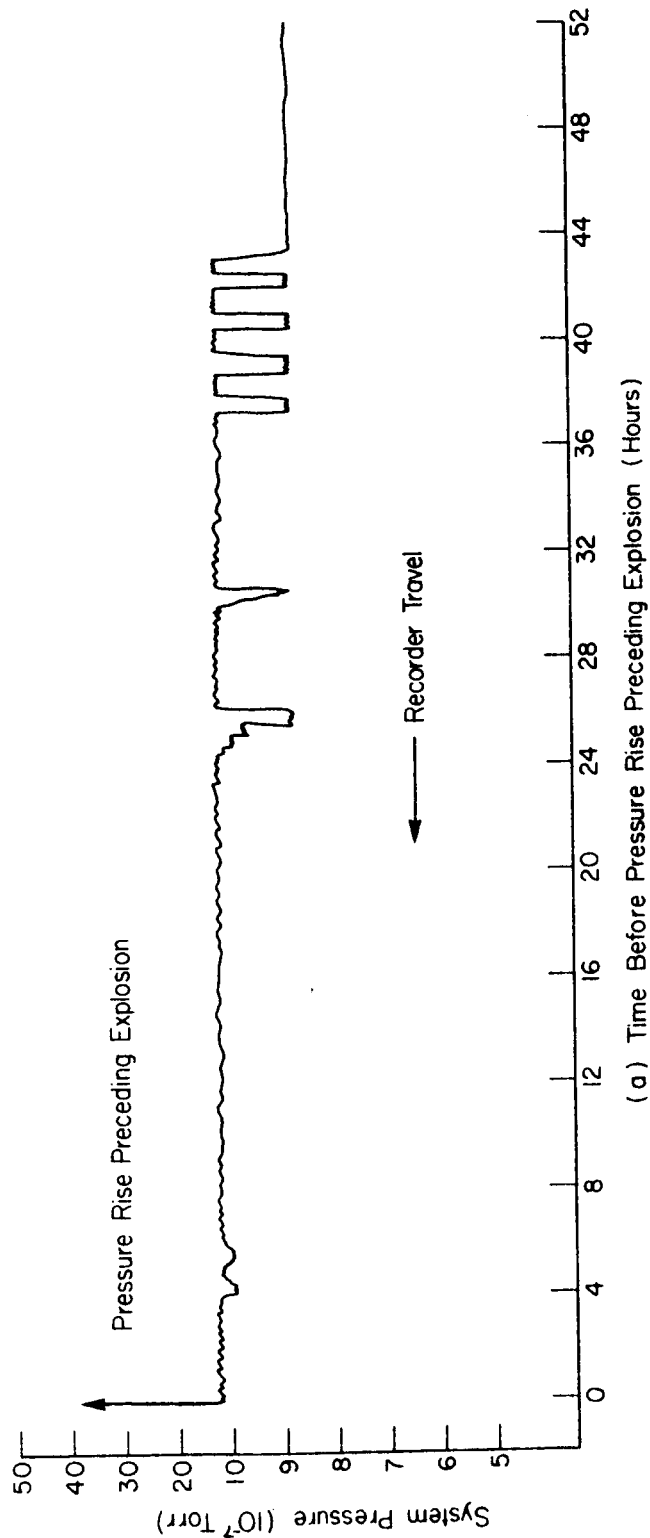


Figure 12 - Diffusion Pump Fluid Temperature and System Pressure From 0 to 52 Hours Prior to Explosion

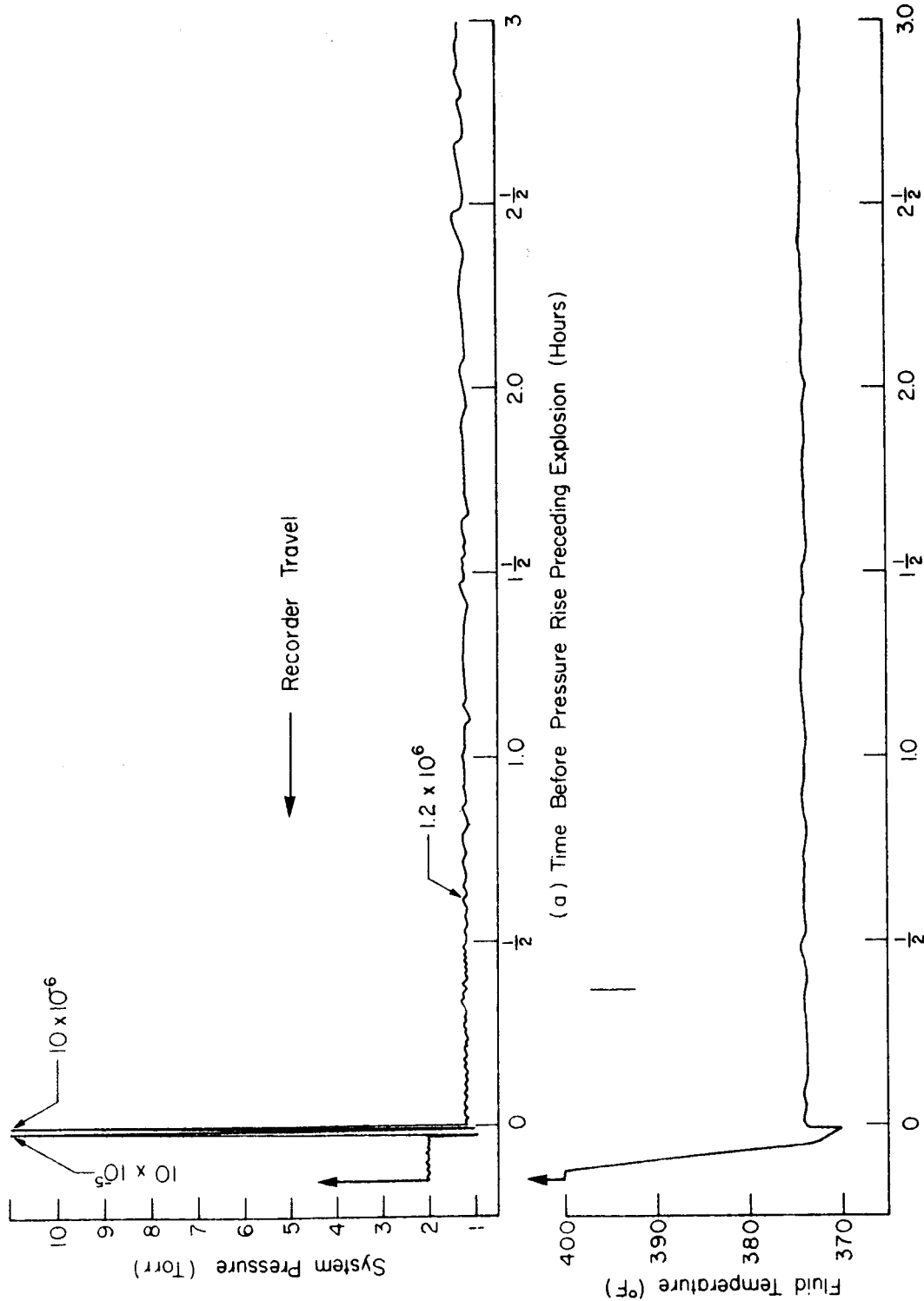


Figure 13 - Diffusion Pump Fluid Temperature and System Pressure From 0 to 3 Hours Prior to Explosion



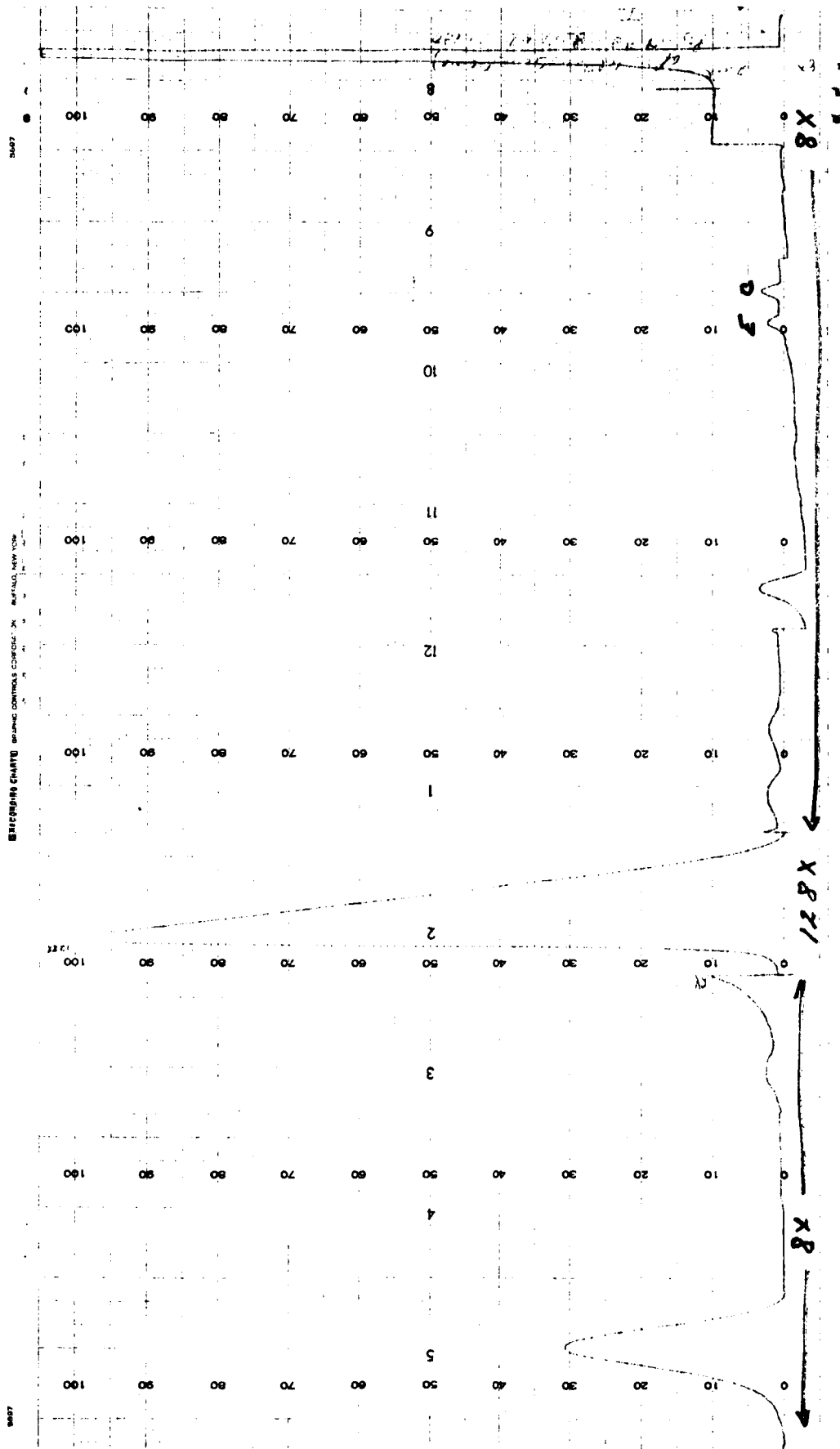


Figure 15 - Gas Chromatogram of DC-704 Fluid After 20 Days of Usage and 7½ Hours of Ozone Leakage into System

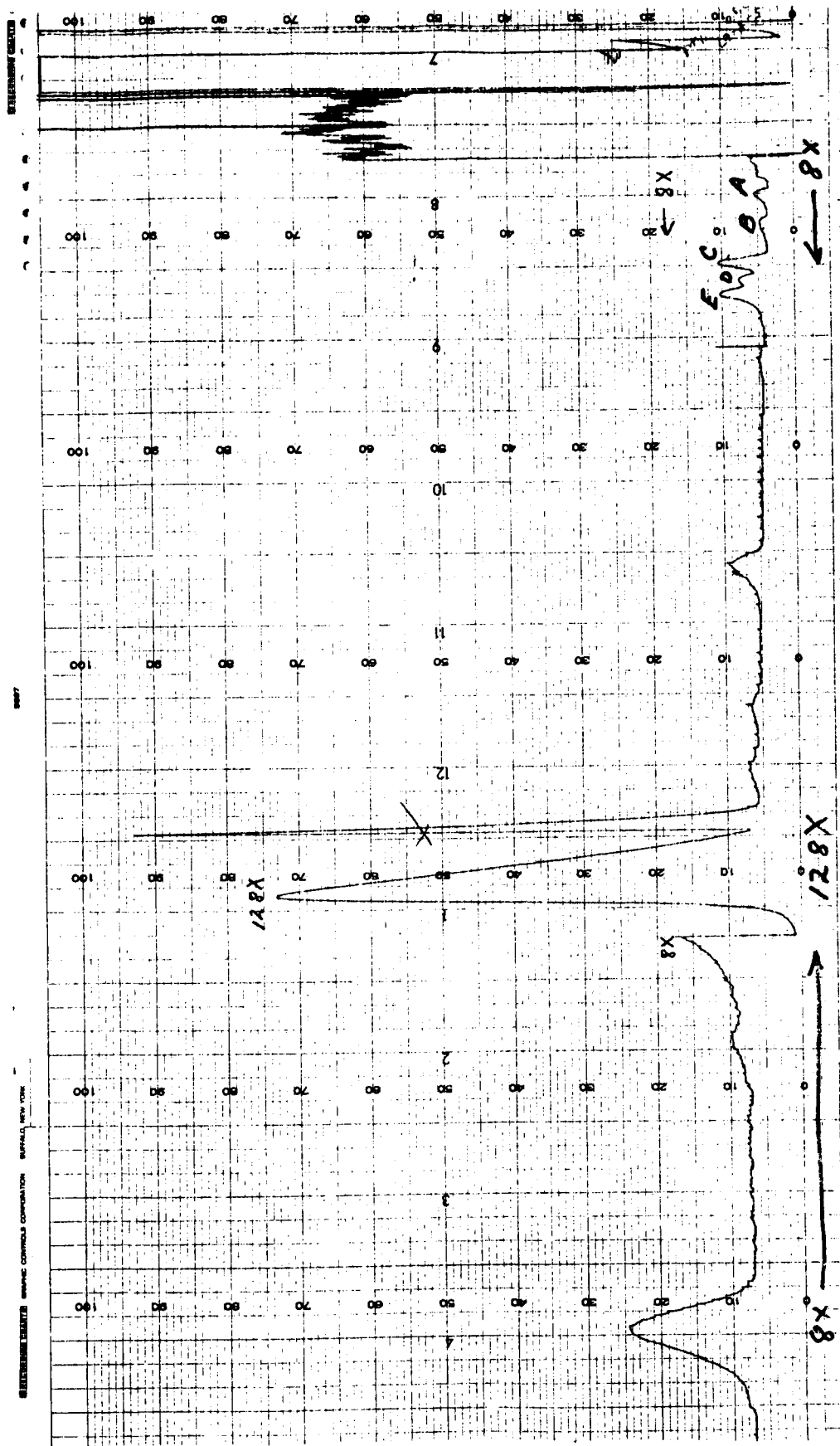


Figure 16 - Gas Chromatogram of DC-704 Fluid After 128 Days of Usage Including 12 Days of Ozone Leakage into the System without Aspirator





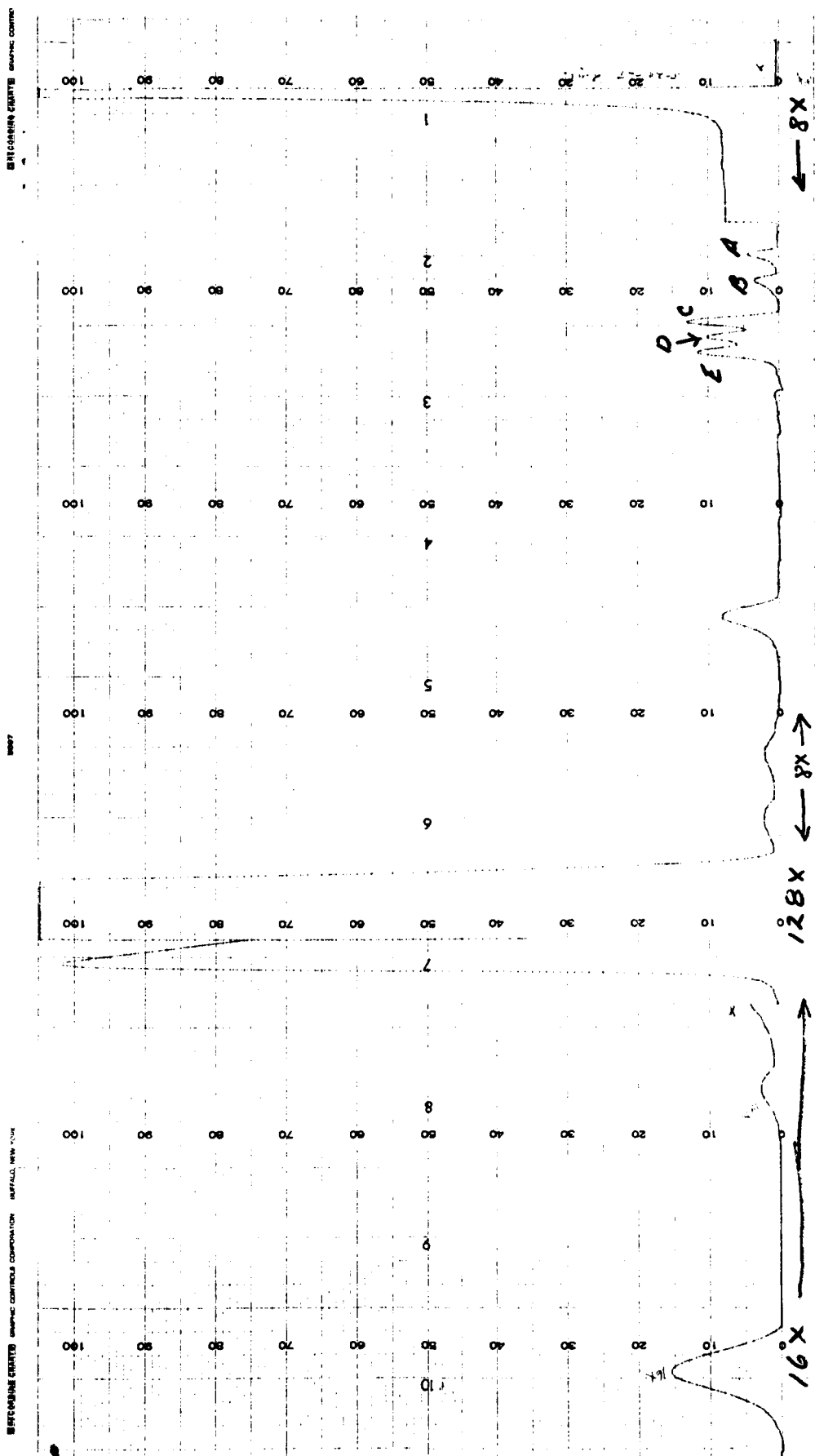


Figure 18 - Gas Chromatogram of DC-704 Fluid Removed 43½ Hours Prior to Explosion

It is not known at present what significance to attach to the appearance of the component, since its identity is unknown. However, it does establish that a change in composition had occurred in the fluid preceding the explosion.

The chromatograms, as presented, do not reveal two additional components in the fluid which elute much later in the chromatograms. These components elute at points 2.7X and 3.9X greater than the major DC-704 component which had an elution time of 37 minutes. Both components were present in the original fluid and were not observed to vary in composition with time to any great extent.

Mass spectrometry studies were attempted on the various components present in the used fluid in order to gain some information as to the nature of the higher components present in the fluid. These analyses, however, were unsuccessful in view of the high bleed rate of the SE-30(silicone gum rubber) substrate which gave a continuous background. The low levels of material isolated from the gas chromatography column could not be clearly defined over the background level.

## 5.0 DISCUSSION

The total accumulated quantity of ozone which was leaked into the diffusion pump vacuum system during the complete 143 day test period is very small. This total leakage would account for only  $8 \times 10^{-7}$  moles of ozone. This is more than 8000 times as much ozone as was leaked into the vacuum system during the previous study when the explosion occurred. However, it may be more significant to point out that approximately 100,000 times more air was leaked into the system than ozone.

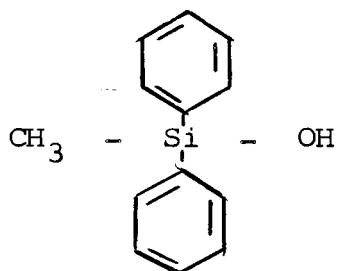
This quantity of air may also have an influence on the stability of DC-704, since it probably contains a large number of oxides generated when the air passed through the corona arc ozone generator. In addition, the air-ozone mixture will contain small amounts of water vapor which are known to contribute to the formation of diphenylmethysilanol.

At present, it is not known what significance the light components and, in particular, component D (see chromatograms) play in the explosion susceptibility of the DC-704 fluid. Certainly one could postulate that this component represents the primary step toward the formation of the thermally unstable and highly reactive intermediate(s) which, if allowed to proceed, can initiate an explosive reaction. Actually, this may very well be the case, but there is certainly no substantiating evidence to either support or rule out this possibility.

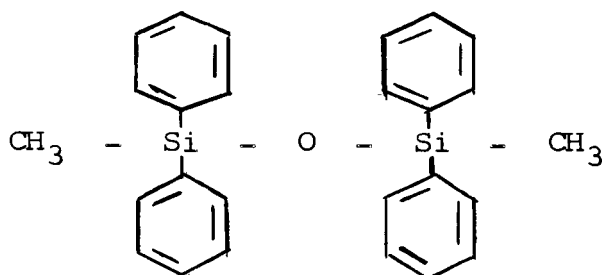
The fact that other light components are also observed in the gas chromatograms would certainly suggest that the diffusion pump fluid is undergoing low order degradation. The grouping of these components in a reasonably close elution point would also suggest that they probably represent a form of the basic structural unit of the fluid and, with slight modifications in structure, could yield small differences in their vapor pressure. Since the doublet (C) and (E) is first to appear followed by the second doublet (A) and (B), the latter doublet may well arise from the initial set. Peak D may be a combination product between either A or B with C or E. Conversely, it may also represent an entity entirely different from either A, B, C, or E.

If for the sake of discussion we consider the four light end component products of DC-704 breakdown, we would predict several possible structures for these components. The one

obvious degradation product could be the diphenylmethylsilanol which would be formed by the presence of moisture in the system,



but could also recombine to form the corresponding siloxane,



However, in a dilute system this reaction would be expected to be slow and the silanol component may exist for a finite time interval before condensing. If the presence of ozone in the system is to mediate an unstable silylperoxide through the formation and cleavage of an intermediate ozonide, the silanol may be the reactant for either hydroperoxide (intermolecular) or peroxide (intramolecular) formation. However, the nature of the ozonide formed at the operating temperatures of a diffusion pump is difficult to postulate.

A second factor which has not been possible to substantiate is the possible influence of hydrocarbons in the overall scheme. Since low levels of volatile hydrocarbons backstreaming from the mechanical pump is always a possibility, this also must be considered as a likely sink for trapping ozone.

In view of the various electrophilic and nucleophilic attacks, one can postulate for the DC-704 fluid under varying conditions of electron delocalization in the siloxane chain it would be almost impossible to predict what course of primary action is involved in the formation of the highly unstable products. To complicate this picture to a greater extent, silicone has five d-orbitals, two of which are capable of forming bonding hybrids of the  $d^2sp^3$  type. Although this

requires a substantial decrease in the electron density of the silicon atom by its linkages to other atoms, the diphenyl substituents may exhibit sufficient electron withdrawing effects to mediate such a structure.

This data is presented only to emphasize the many possible results available for consideration in postulating an interpretation of the results. Only through a detailed study with "model" systems can such mechanisms be advanced to any degree of certainty.

However, based on the results accumulated during this investigation, the following mechanisms would appear most probable. The attack of ozone to form an unstable ozonide intermediate. This formation proceeds via an ionic mechanism and would not be expected to initiate a free radical reaction with the fluid. However, ozonide degradations can proceed by the reactions presented in the final report\* of the previous program to form hydroperoxides, peroxides or polyperoxides, which in breakdown can initiate a free radical mechanism. This mechanism would result in a disproportionation reaction in the DC-704. Such a disproportionation would result in the spontaneous liberation of large quantities of methane and/or volatile aromatic species which can account for the rapid increase in pressure (explosion).

The disproportionation reaction of the DC-704 would initially take the form of a polymerization reaction and proceed to disproportionation at an accelerated rate on the accumulation of sufficient free radicals. The formation of carbon residue could result from exposure to the atmosphere.

Although it cannot be said that this explosion completely duplicates the explosion generated on the previous program, it must be assumed the ozone had a significant influence on both occurrences. Complete duplication of any explosive reaction is difficult; however, duplication of an ozonolysis even under very closely controlled low temperature conditions is extremely difficult. As was discussed previously, the exact mechanism by which ozone could initiate an explosive reaction could follow several alternate paths, particularly at elevated temperatures. Therefore, the difference in the length of time ozone was leaked into the system during the present study as opposed to the previous study may be attributed to the initiating step. This initiation can be influenced by the composition of the fluid. The presence of

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\* NASA Contract No. NAS5-9632 entitled, "Investigation of the Explosion Hazard of Contaminated Diffusion Pump Fluids," Page 60.

very trace reactive species could radically alter the rate of ozonolysis. These species in one system could be unsaturated hydrocarbons introduced by backstreaming from the mechanical pump. Alternatively, over a longer period of time this reaction could proceed by direct attack on DC-704.

## 6.0 RECOMMENDATIONS

Further studies should be conducted to determine the mechanism or mechanisms by which ozone will generate an explosive reaction in DC-704 fluid. These studies would investigate the compatibility of the DC-704 fluid and the individual components present in the fresh and used fluid with ozone and peroxides. Such studies would be conducted under ideal conditions in order to determine rates of reaction, types of products formed, influencing factors such as temperature and trace levels of impurities, and ultimate stability.

Once the conditions surrounding the initiation of instability in DC-704 are determined, their relation to an actual operating diffusion pump or to other diffusion pump fluids can be either predicted or experimentally evaluated. However, until more is known concerning the basic effect of ozone in DC-704, it will be very difficult to predict the relative stability of any system where ozone is present or to suggest protective schemes which may be advantageous in systems such as man rated chambers.